Strategic Design and Optimization of Inorganic Sorbents for Cesium, Strontium and Actinides

SRNL™
SAVANNAH RIVER NATIONAL LABORATORY

We Put Science To Work

David Hobbs

Presented at the EMSP High Level Waste Workshop
January 19, 2005

EMSP
Environmental Management Science Program

SRNL-LWP-2005-00004

Co-Principal Investigators

- May Nyman – Sandia National Laboratories
- Abraham Clearfield – Texas A&M University
- Ed Maginn – University of Notre Dame

Outline

- Goals
- Benefits
- Research Strategy
- Findings
- Research Plans
- Acknowledgements

Goals

- Determine the structural factors of inorganic-based sorbents and ion exchange materials that control selectivity and kinetics for the removal of cesium, strontium and actinides from strongly alkaline waste solutions

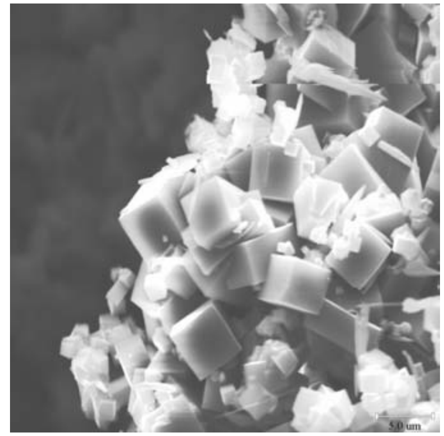
- Apply that understanding to the synthesis of materials with improved cesium, strontium and actinide removal characteristics

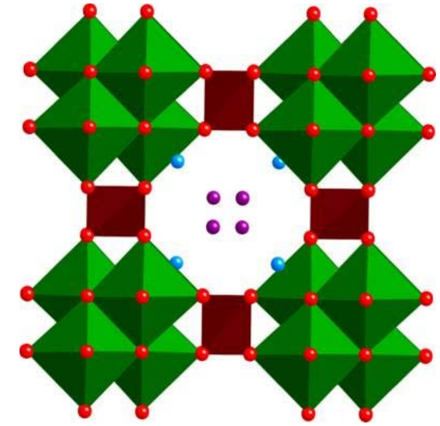
Benefits

- Improved radiochemical separations
- Increased throughput
- Reduced solids handling
- Simplified radiochemical separation flowsheet

Research Strategy

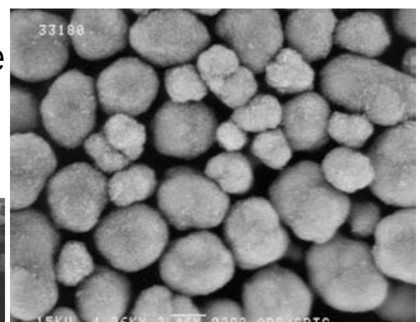
- Synthesize and measure ion exchange characteristics of titanosilicate, titanate and polyoxometalate materials
- Determine solid state structures of IX materials
- Develop molecular models of IX materials
- Use molecular models to guide synthesis of new IX materials

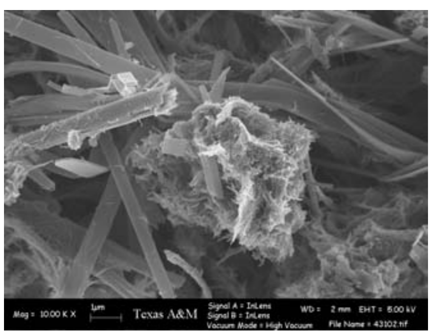




crystalline silicotitanate
$Na_2Ti_2O_3(SiO_4)\cdot 2H_2O$ (CST)

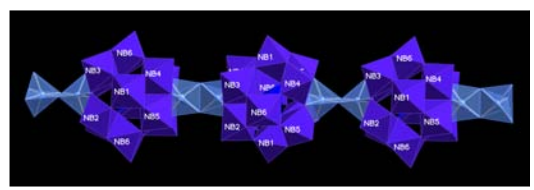
monosodium titanate
$NaTi_2O_5H$ (MST)

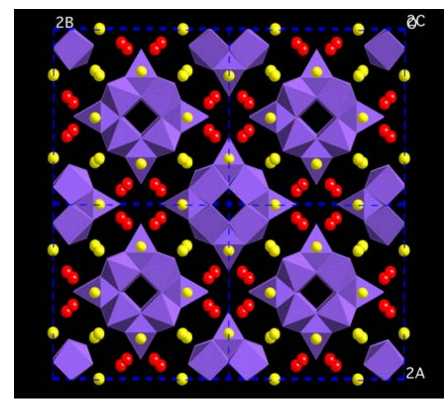




sodium nonatitanate
$Na_4Ti_9O_{20}\cdot xH_2O$ (SNT)

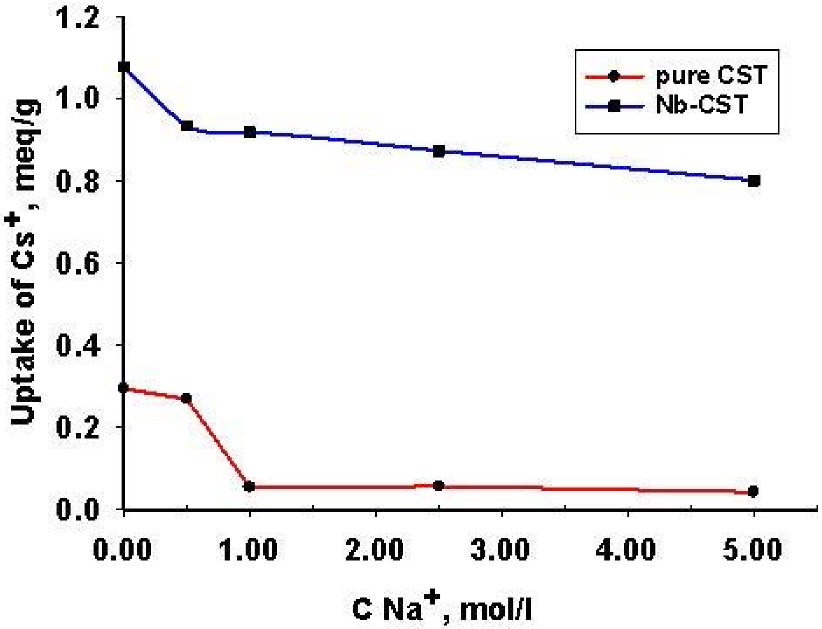
Polyoxometalate (IPX)
$M_{12}[Ti_2O_2][SiNb_{12}O_{40}]\bullet 16H_2O$
where M = Na, K





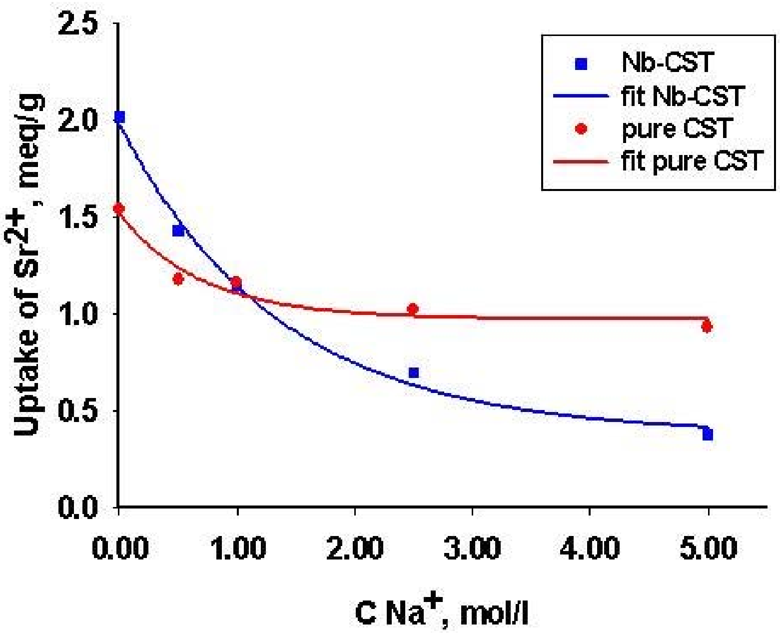
Research Findings

Crystalline silicotitanate (CST)



Substitution of Nb for Ti in framework significantly enhances Cs selectivity

Strontium uptake decreases with increasing ionic strength; influence greater for Nb-CST

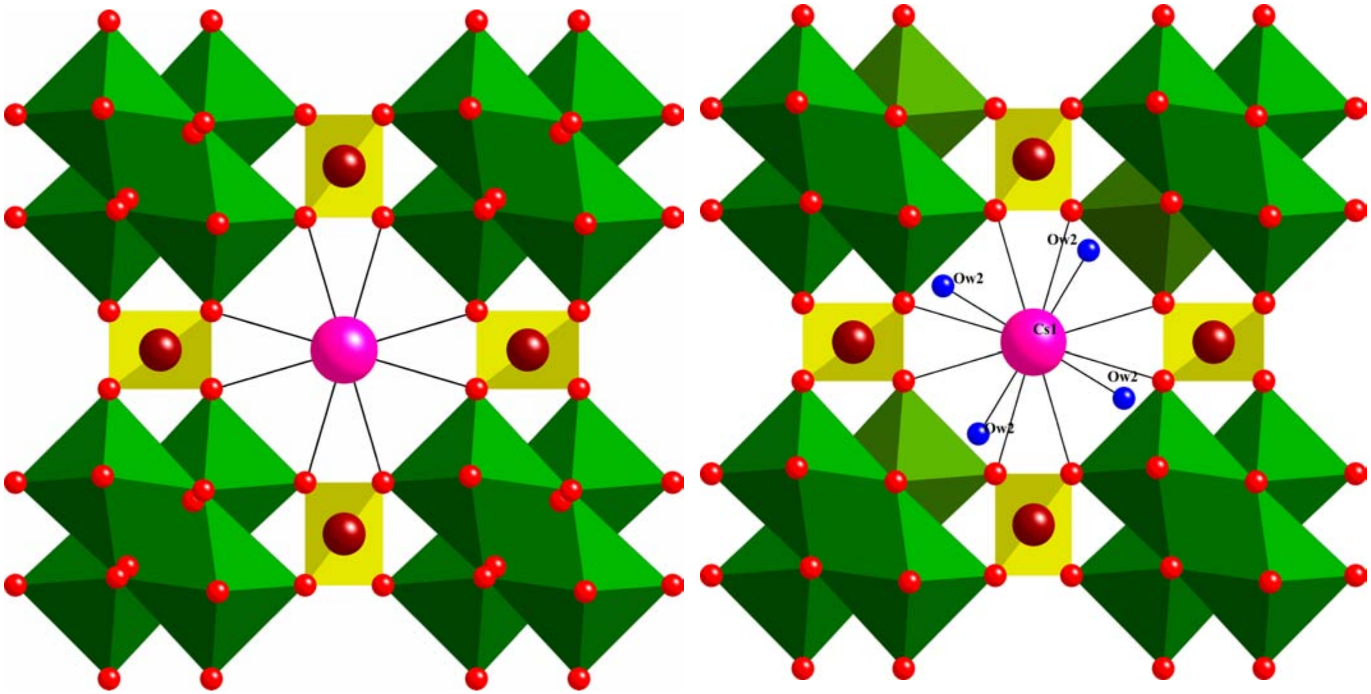


SRNL

Cs Exchanged CST

CST

Nb-CST



CN = 8

CN = 12

Less Na in tunnel with Nb-CST

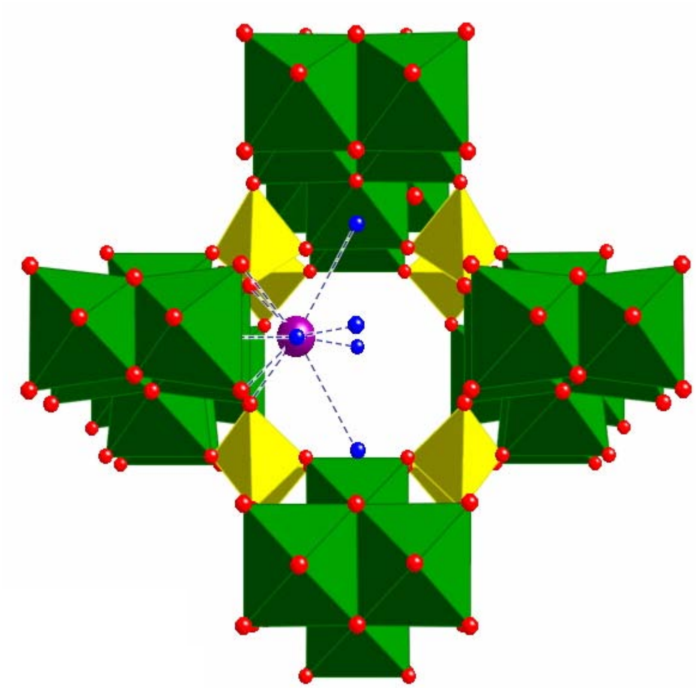
Increased cesium coordination in Nb-CST

Molecular models of CST and Nb-CST agree well with XRD studies

A. Tripathi, D. G. Medvedev, M. Nyman, A. Clearfield ; J. Solid State Chem., 175, 72-83, 2003

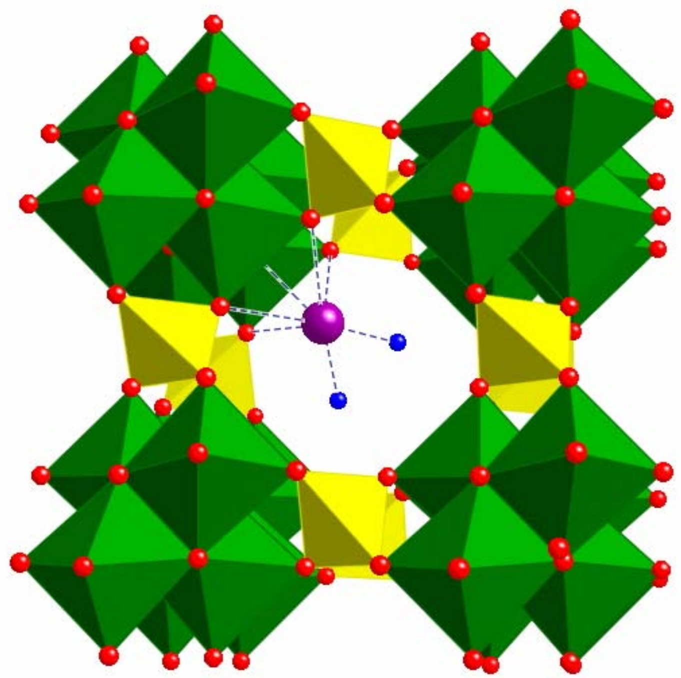
Sr Exchanged CST

CST



CN = 10

Nb-CST



CN = 7

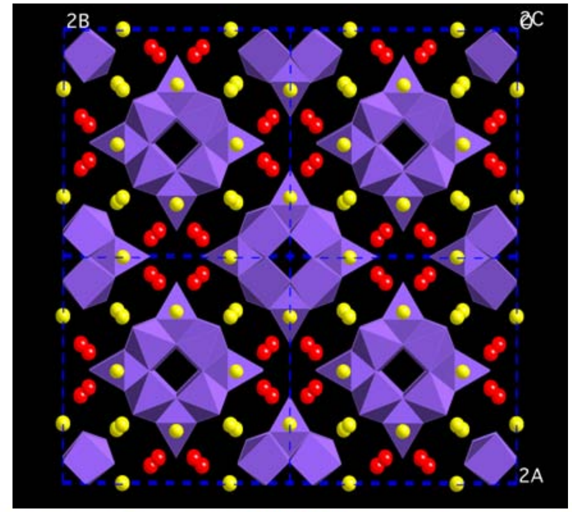
Reduced affinity for Sr with Nb-CST due to lower degree of coordination

A. Tripathi, D. Medvedev, A. Clearfield; Journal of Solid State Chemistry, in press

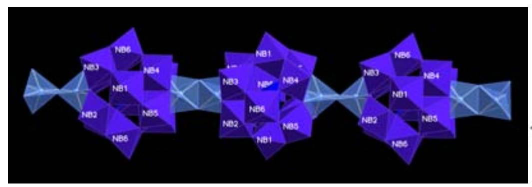
SRNL

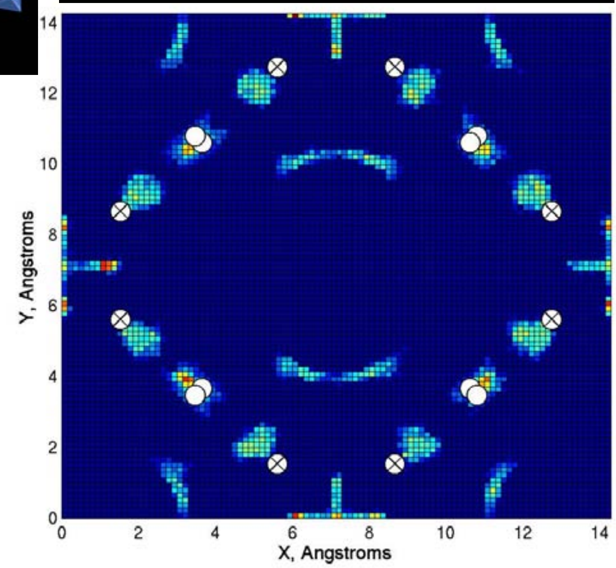
Na-IPX Model

- 40 possible sites per unit cell
- Charge neutrality requires 24 Na^+ per unit cell
- XRD cannot distinguish Na^+ and H_2O
- Molecular modeling indicates 4 sites



Site #	Na Occupancy (%)
1	100
2	98.1
3	53.7
4	7.8



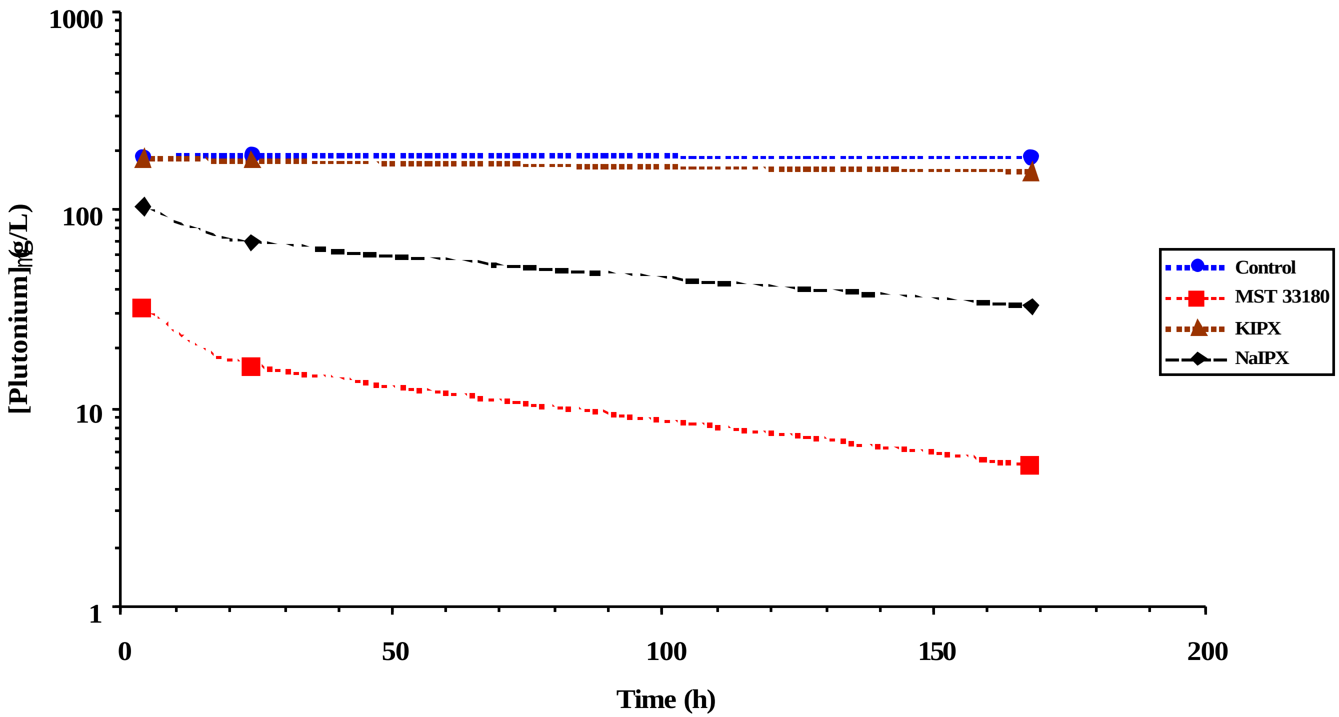


- Water diffusely located near Sites 2, 3 & 4
- Good agreement between predicted H_2O content and weight loss measured by TGA
- Substitution of Nb for Ti reduces Na^+ population in Site 3

Bonhomme, Larentzos, et al., Inorganic Chem., in press.

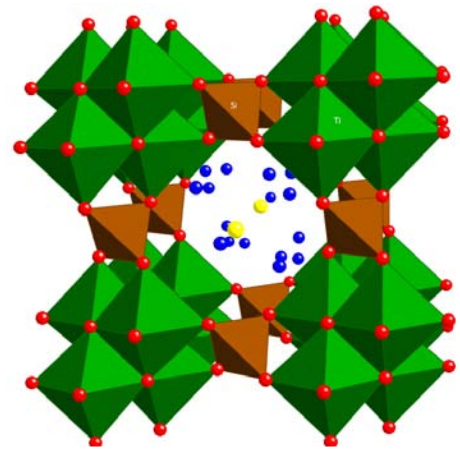
Performance of Keggin Chain Materials

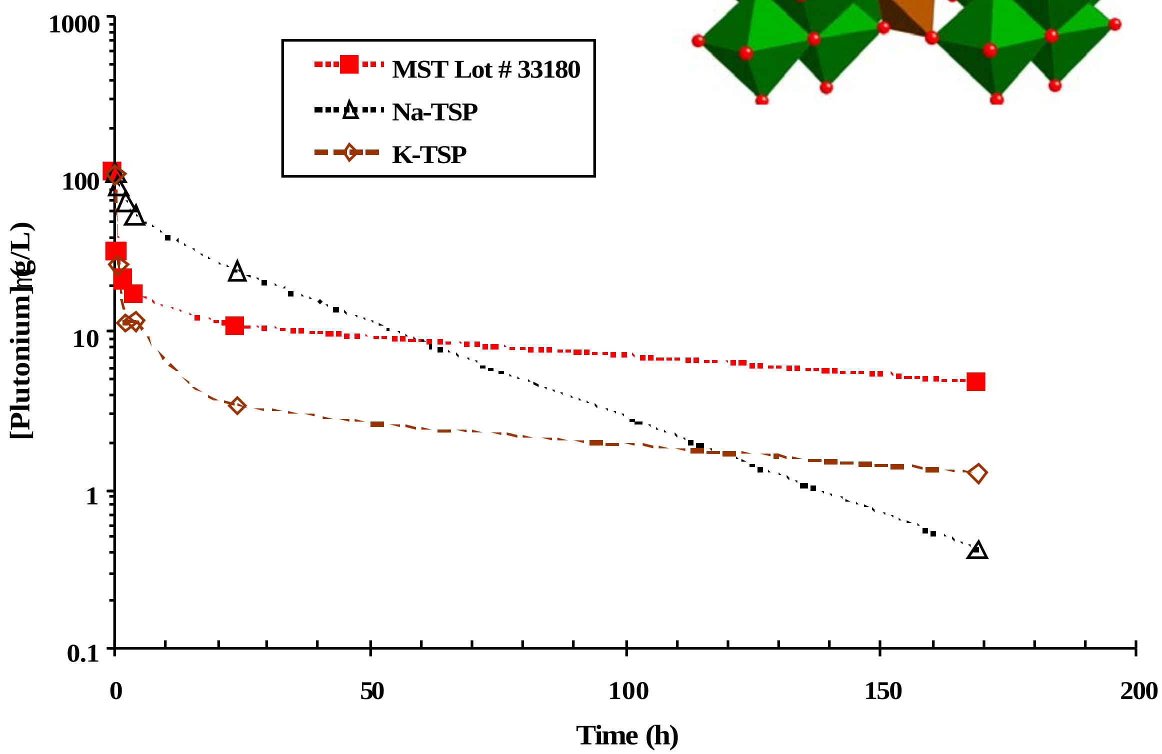
- Keggin chain (IPX) materials remove Sr & actinides
- Not as effective as MST
- Na-IPX more effective than K-IPX



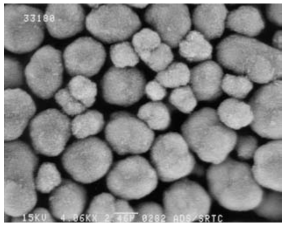
Titanosilicates with Pharmacosiderite Structure (TSP)

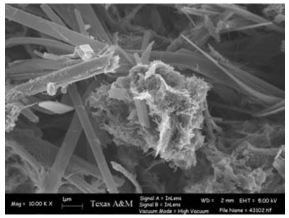
- $M_3H(TiO)_4(SiO_4)_3 \bullet xH_2O$
  M = Cs^+, Na^+, K^+, Sr^{2+}
- TSP materials do not exchange Cs^+ in HLW media, but do exhibit excellent Sr & actinide removal
- Sr removal faster with Na-TSP
- Pu removal faster with K-TSP





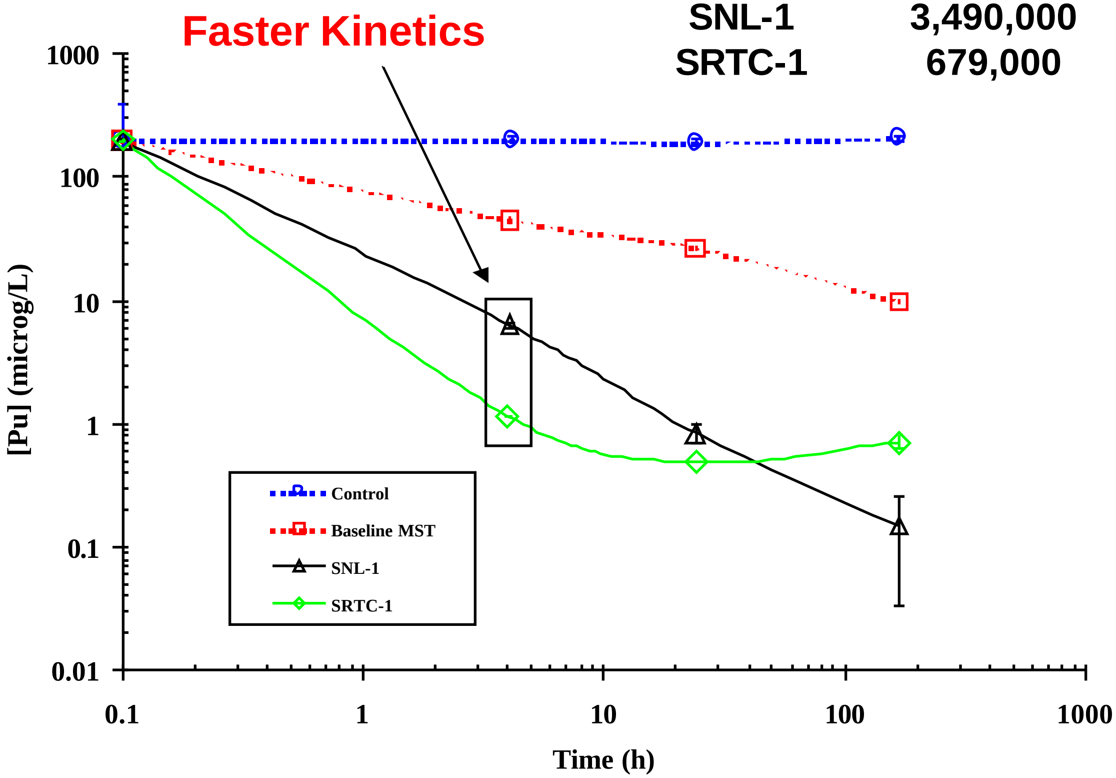
Sodium Titanate Materials





Increased Capacity

Sample	168-hour K_d (mL/g)
Baseline MST	50,300
SNL-1	3,490,000
SRTC-1	679,000



- Excellent affinity for Sr & actinides, but not Cs in HLW solutions
- Investigate methods to modify morphology
  - chemically modified MST exhibits significantly improved Sr/actinide removal performance (EM-21)
  - decreased SNT crystallinity improved Sr/actinide removal

Research Plans

- Identify actinide binding sites for the TSP, Keggin and SNT materials
  - XRD
  - XAFS
- Complete development of and use molecular models for the design of new derivatives of CST, Keggin, TSP and SNT materials
  - Calculation of water isotherms
  - Calculation of selectivity and distribution coefficients for Cs^{+}, Sr^{2+} and UO_2^{2+} versus Na^{+} in materials with various framework substitutions
  - Investigate Quench Simulation and Reverse Monte Carlo methods to model amorphous materials

Research Plans

- Synthesize, characterize and test performance of new derivatives of SNT/MST, CST, TSP, Keggin and trisilicate materials
  - Mixed phase SNT/CST
  - Metal-substituted TSP (e.g., Ge for Si)
  - Cationic layered materials intercalated with anionic polyoxometalates
  - Polyoxometalates materials with alternate counterions
  - Modified SNT/MST materials
- Test performance of promising new materials with actual tank waste solutions (SRS)

Acknowledgements

- SRNL
  - M. Duff, M. Blume, L. Thacker, D. DiPrete,C. DiPrete
- SNL
  - S. Thoma, L. Neidel, L. Lybarger, A. Sanchez, F. Bonhomme, T. Alam, M. Rodriguez, B. Cherry, J. Krumhansl, T. Nenoff, A. Sattler
- Texas A&M
  - A. Tripathi, D. Medvedev
- Notre Dame
  - J. Larentzos
- Georgia Institute of Technology
  - J. Bradley, Z. Dai
- Argonne National Laboratory
  - N. Dietz, J. Fortner
- Pennsylvania State University
  - K. Mueller